Synthesis of nanostructured materials (04)

Most of the chemical methods are cost effective, but their full potential for [illegible] device-quality films has not been completely explored in many cases.

6.5 SOL-GEL PROCESS

soft milk of magnesia paints

It is a bottom-up approach of synthesis which is in use since late 1800s. The modern sol-gel technique started around 1970s. It is an example of liquid phase synthesis. A sol is a colloidal or molecular suspension of solid particles or ions in a solvent. A gel is a semi-rigid mass that forms when the solvent from the sol begins to evaporate and the particles or ions left behind begin to join together in a continuous network. Sol-gel is a multi-step chemical solution process (i.e. a wet chemical technique) widely used recently in the fields of materials science and ceramic engineering to make ceramic and glass materials in the form of thin films, fibers, or powders.

The process of sol-gel generally starts with the mixing of metal alkoxides or salts in water or in a suitable solvent (in most cases alcohol) at ~~ambient or~~ slightly elevated temperatures. Thus metal alkoxides and metal chlorides are typical precursors in this process which undergo hydrolysis and polycondensation reactions. The most widely used are tetramethoxysilane (TMOS), and tetraethoxysilanes (TEOS) which form silica gels. Alkoxides are immiscible in water. They are organometallic precursors for silica, aluminum, titanium, zirconium and many others. In the process metal-oxo or metal-hydroxo polymers are formed.

In sol-gel process it is very important to control the pH of the starting solution to avoid the precipitation as well as to form the homogeneous gel, which can be achieved by the addition of base or acidic solutions. Organic compounds with hydrophilic functional groups in small molecules such as citric acid, succinic acid, oxalic acid, tartaric acid etc. and polymers (e.g. polyacrylic acid and polyvinyl pynolidine) can be used with metal ion sources to form the sol as well as control the particle size and uniformity of the products. A catalyst is used to start the reaction and control pH of the solution.

Sol-gel formation occurs in four stages:

1. Hydrolysis
2. Condensation
3. Growth of particles
4. Agglomeration of particles.

These processing steps are discussed below :

Hydrolysis : In hydrolysis, addition of water replaces alkoxy groups [OR] with hydroxyl groups [OH]. Hydrolysis occurs by attack of oxygen on silicon atoms in silica gel. A catalyst such as HCl and NH_3 accelerates the hydrolysis. Hydrolysis

...continues until all [OR] groups are replaced by [OH-] groups. Subsequent condensation involving silanol group (Si-OH) produced siloxane bonds (Si-O-Si), alcohol and water.

Condensation : Polymerization to form siloxane bond occurs by either a water producing or alcohol producing condensation reaction. Condensation reaction finally results in the formation of monomer, dimer, cyclic tetramer, and high order rings. Hydrolysis rate is influenced by pH, reagent concentration and H_2O/Si molar ratio. Ageing and drying are also important steps. By controlling these factors the structure and properties of sol-gel derived inorganic networks can be varied.

Growth and Agglomeration : With increase in the number of siloxane bonds, the molecules aggregate in the solution, where they form a network and then a gel is formed upon drying. The water and alcohol are driven off and the network shrinks. For pH values greater than 7 and H_2O/Si value ranging from 7 to 5, spherical nanoparticles are formed. The reactions involved are as follows:

$$2\,HOSi(OR)_3 \longrightarrow (OR)_3\,SiOSi(OR)_3 + H_2O$$

or

$$2\,HOSi(OR)_3 \longrightarrow (OR)_2OH\,Si\,O\,Si\,(OR)_3 + H_2O$$

For pH > 7, silica is more soluble and silica particles grow in size. The growth of particles stops when the difference in solubility between the smallest and largest particles becomes indistinguishable. **Higher temperatures result in the formation of larger particles.**

Advantages of Sol-Gel Technique

- Sol-gel method of thin film deposition is a cheap and low temperature technique with fine control on the chemical composition of the product.
- It is able to produce high purity products because the organo-metallic precursor of the desired ceramic oxides can be mixed, dissolved in a specified solvent and hydrolyzed into a sol, and subsequently a gel.
- By this process we can get at low temperature high density glass without high temperature re-crystallization.
- Smaller particle size and morphological control in powder synthesis.
- It can produce thin bond coating to provide excellent adhesion between the metallic substrate and the top coat.
- This process is able to coat onto large or complex shape objects.
- Sol-gel process can produce thick coating to provide corrosion protection performance.
- This process can have low temperature sintering capability, usually in the range 200-600°C
- Sol-gel is a versatile process as it can produce aerogels, xerogels, ceramic materials, nanopowders, nanorods and nanostructured thin films etc.

Disadvantages of Sol-Gel Technique

- The cost of the raw materials (i.e. chemicals) may be high as compared to mineral based metal ion sources.
- Products would contain high carbon content when organic reagents are used in preparative steps and this would inhibit densification during sintering.
- There is often a large volume shrinkage and cracking during drying due to the generation of large capillary stresses.
- It is difficult to avoid residual porosity and OH-groups
- Being a multi-step process, close monitoring is required
- The process is not very clean. It contains undesired atoms, molecules, ions etc. This deteriorates electrical and optical properties of deposited material.
- pH and precipitation.

Applications

- Sol-gel process has been extensively used for forming coatings on window glass
- It can be used to produce powders and fibers
- Sol-gel technique can be used to deposit films and coatings on a range of different surfaces, enabling a flexibility which is not available in many vapour phase methods
- It is used in drug delivery systems
- In making ultraviolet (UV) protection gels
- For producing lubricants and scratch free paints
- In developing new fire retardant materials.

6.6. ELECTRODEPOSITION

Electrodeposition is a liquid phase chemical method of synthesis of nanostructured materials. It belongs to the category of bottom-up approach of synthesizing nanomaterials. Thin films have been extensively used in microelectronics. There are numerous and growing applications in communications, optical electronics, coatings of all kinds and in energy generation. Electrodeposition is a long established method to deposit metal layers on a conducting substrate. Ions in the solution are deposited onto the negatively charged cathode, carrying charge at the rate which is measured in the form of a current in the external circuit. The layer thickness is a function of current density and the time for which the current flows. The deposit can be detached if the substrate is chosen to be soluble by dissolving it away (*Fig. 6.3*).

Electrodeposition is the most suitable technique for depositing nanostructured thin films from aqueous solution served as samples under investigation. It is particularly suited to the fabrication of heterojunctions simply through a change in the deposition electrolyte. Electrodeposition of metallic layers